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(54) INORGANIC-ORGANIC COMPOSITES AND METHODS OF REACTING THE SAME WITH ORGANO-TITANIUM COMPOUNDS

(71) We, KENRICH PETROCHEMICALS, INC., a corporation of the State of Delaware, one of the United States of America, East 22nd Street, Bayonne, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

Inorganic materials have long been used as fillers, pigments, reinforcements and chemical reactants in polymers. They are essentially hydrophilic, i.e., easily wetted by water or able to adsorb water. However, their compatibility with polymers is limited. Therefore, poor utilization is obtained of the potential reinforcement, of color or opacity, or chemical reactivity of inorganic materials.

For example, zinc oxide is a commonly used component in rubber compounds. When comminuted zinc oxide is added to a rubber compound as a dry powder, it is difficult to disperse it completely in the rubber. On the other hand, predispersion of the zinc oxide in an organic medium which is a plasticizer for the rubber forms a stiff paste which is not dusty, is easy to weigh, and aids in the dispersion in the rubber.

Likewise, other comminuted inorganic solids such as magnesium oxide, calcium oxide, other metal oxides, and fillers such as clay, calcium carbonate, colloidal silica and carbon black may be predispersed in an organic plasticizer or polymer prior to addition to a rubber or plastic compound.

Organo-titanium compounds are well known. A wide variety may be prepared from tetraalkyl ortho titanates by reaction with organic acids, as for example in U.S. Patent 2,621,193.

Organo-titanates having *di-* or *tri-* alkyl hydrolyzable groups and with, therefore, only one or two organic groups which are non-hydrolyzable have been used to treat the surfaces of inorganic materials in order to render them hydrophilic, as for example in U.S. Patent 3,660,134. Such *di-* or *tri-* alkyl hydrolyzable titanates form a multi-molecular layer or envelope around the inorganic particles, resulting in less efficient use of the organo-titanate, as well as a weaker bond between the inorganic particle surface and the organic continuous phase.

The reaction is accomplished by adding the organo-titanate to a suspension of the inorganic material in an inert solvent such as naphtha, trichloroethylene, toluene or hexane. After the reaction is completed, the solvent is removed and the treated, dried inorganic material is subsequently incorporated in an organic

polymer system. U.S. Patent 3,697,475, for example, incorporates such treated inorganic fillers in thermoplastic polymer films.

According to the present invention there is provided a mixture of organo-titanates represented by the formula $Ti(OR)_{4-m}(OCOR')_m$ wherein the or each OR is a hydrolyzable group as hereinafter defined, the or each OCOR' is a non-hydrolyzable group as hereinafter defined at least one OCOR' group having from 6 to 24 carbon atoms, and n is more than 3 but not greater than 3.5, the mixture including at least some of one or more of the compounds represented by the formula $Ti(OR)_{4-m}(OCOR')_m$ where m is an integer of from 1 to 3.

By "hydrolyzable" is meant a group which will cleave in an aqueous solution having a pH of about 7 at a temperature of less than 100°C. Hydrolysis may be determined by analysing for liberated acids and alcohols. By "non-hydrolyzable" is meant a group which will not cleave under the aforesaid conditions.

Preferably the value of n in the above formula is between 3.1 and 3.25.

The present invention also provides a composition comprising a comminuted inorganic material and an organo-titanate mixture as defined above or a titanate of the formula $Ti(OR)(OCOR')$, where OR and OCOR' are as defined above, the surface of the inorganic material having been reacted with the titanate mixture or titanate. The present invention further provides a process for producing a dispersion of a comminuted inorganic material in a polymeric medium which comprises admixing an inorganic material, a mixture of organo-titanates as defined above or a titanate of the formula $Ti(OR)(OCOR')$, where OR and OCOR' are as defined above and a polymeric medium, to form a dispersion of the inorganic material, the surface of which has been reacted with said organo-titanate, in the polymeric medium. The amount of the organo-titanate mixture required is preferably at least 0.1 part, more preferably 0.5 to 10 parts, per 100 of the inorganic solid. The reaction takes place on the surface of the inorganic solid, whereby the hydrolyzable group is removed and a bond is established, thus forming an organic, hydrophobic surface layer on the inorganic solid. The inorganic solid, prior to surface modification, is difficult to disperse in an organic medium because of its hydrophilic surface. However, when the organo-titanium compound is incorporated into an organic medium (low molecular weight liquids or higher molecular weight polymeric solids), preferably a rubber medium, the surface of the inorganic solid is wet-out, agglomerates are readily broken into individual particles, and a dispersion having improved properties is formed. Alternatively, the organo-titanate may be first reacted with the organic solid in the absence of an organic medium and thereafter admixed with the latter.

The method of the present invention converts the surfaces of inorganic materials from a hydrophilic to a hydrophobic state preferably by reaction in an organic medium. This preferred procedure eliminates the prior art intermediate steps of dispersing the inorganic material in a solvent, reacting, filtering and drying the inorganic solid before dispersing it in a polymer.

By means of the present invention, the dispersion of inorganic materials in organic polymer media is improved in order to obtain: (1) lower viscosity or higher loading of the dispersate in the organic medium; (2) higher degrees of reinforcement by the use of fillers, thereby resulting in improved physical properties in the filled polymer; (3) more complete utilization of chemical reactivity, thereby reducing the quantity of inorganic reactive solids required; (4) more efficient use of pigments and opacifiers; (5) higher inorganic-to-organic ratios in a dispersion, and (6) shorter mixing times to achieve dispersion.

Also, according to the invention herein, the reaction with the single hydrolyzable group of the organo-titanate may be carried out neat or in an organic medium to form a liquid, solid, or paste-like solid dispersion which can be used in the compounding of the final polymeric system. Such dispersions are very stable, i.e., having no tendency to settle, separate, or harden on storage to a non-dispersible state.

Moreover, the invention simplifies the making of inorganic dispersions in organic media by providing a means to eliminate the solvent, to reduce the cost of processing equipment, and to reduce the time and energy required to disperse an inorganic solid material in a liquid or polymeric organic solid.

The present invention results in the formation of a reinforced polymer which has a lower melt viscosity, improved physical properties, and better pigmentation characteristics than are displayed in prior art materials.

The practice of the present invention achieves a product comprising natural or synthetic polymers which contain particulate or fibrous inorganic materials

which reinforce, pigment, or chemically react with the polymer to produce a product having superior physical properties, better processing characteristics, and more efficient utilization of pigments.

Amongst the advantages gained by the practice of this embodiment of the present invention is the dispensing with the use of volatile and flammable solvents as required in the prior art. Thus, it is not necessary to dry the filler or to recover solvents. Furthermore, there is no possibility of a multi-molecular layer formation since there is only one hydrolyzable group in the organo-titanate reactant. Also, the practice of the present invention results in a non-oxidizing dispersion.

The preparation of illustrative organo-titanium compounds is described in U.K. Patent Specification No. 733,224. While many of the compounds of the basic starting material $Ti(OR)_4$ may be used in preparing the polyesters, from the viewpoint of reactivity and economy, tetraisopropyl titanate is preferred. Referring to the above formula, R, which forms part of the hydrolyzable group, is preferably a straight chain, branched or cyclic alkyl group having from 1 to 5 carbon atoms per molecule. The groups include methyl, ethyl, n- and isopropyl, n-, sec-, and t-butyl, pentyl and cyclopentyl.

With regard to the non-hydrolyzable groups (OCOR'), they are all preferably formed from organic acids having 1 to 50 carbon atoms, and at least one has from 6 to 24 carbon atoms, such as stearic, isostearic, oleic, linoleic, palmitic, lauric and tall oil acids. Isostearic acid is particularly advantageous because it forms a triester that is a liquid at room temperature, which is more readily soluble in organic media. A major consideration is the total number of carbon atoms in the non-hydrolyzable groups. The sum of the carbon atoms in the three R' groups for the component of the mixture $Ti(OR)(OCOR')$, is preferably at least 15. Furthermore, as indicated above at least one R' group must have a long chain by which is meant a group having from 5 to 23 carbon atoms in order to give the necessary viscosity reduction to the reaction product of the organic titanate and the organic material. As an example, two R' groups may be isopropyl and the long chain R', lauryl. Materials which can be readily liquefied or dissolved at conventional mixing temperatures are most desirable. Equivalent polytitanates may also be used.

Preferably, the R' groups are alkyl groups having up to 23 carbon atoms; alkenyl groups having up to 18 carbon atoms; or aryl, alkaryl, or aralkyl groups having up to 23 carbon atoms. Additionally, the aforesaid groups may be substituted with halo, nitro, amino, carboxyl, epoxy, or hydroxyl ether or ester groups. Generally from 1 to 6 of such substitutions may occur. Still further, the R' group may contain intermediate hetero-atoms such as oxygen, sulfur or nitrogen in the chain.

All of the R' groups in the organo-titanate compound need not be the same. They may be mixtures of two or more groups, the preparation of which shall be readily understood by those skilled in the art. For example, the $Ti(OR)_4$ starting material may be reacted with two or more organic acids.

The selection of the R' groups for the organo-titanate depends on the particular application. The optimum groups depend on the filler and the monomeric or polymeric organic material, and the desired properties of the filled material. One skilled in the art may determine suitable organo-titanates for specific applications by limited experimental work in light of the teachings herein.

Examples of the R' groups are numerous. These include straight chain, branched chain and cyclic alkyl groups such as hexyl, heptyl, octyl, decyl, dodecyl, tetradecyl, pentadecyl, hexadecyl, octadecyl, nonadecyl, eicosyl, docosyl, tetracosyl, cyclohexyl, cycloheptyl and cyclooctyl. Alkenyl groups include hexenyl, octenyl and dodecenyl.

Groups derived from saturated and unsaturated fatty acids are also useful. In these cases the OCOR' group may be caproyl, caprylyl, capryl, lauryl, myristyl, palmityl, stearyl, arachidyl, behenyl, lignoceryl, dodecylenyl, palmitoleyl, oleyl, ricinoleyl, linoleyl, linolenyl, and gadoleyl.

Halo-substituted groups include bromohexyl, chlorooctadecyl, iodotetradecyl and chlorooctahexenyl. One or more halogen atoms may be present, as for example in difluorohexyl or tetrabromooctyl. Ester-substituted aryl and alkyl groups include 4-carboxyethylcapryl and 3-carboxymethyltoluyl. Amino-substituted groups include aminocaproyl, aminostearyl, aminohexyl, aminolauryl and diaminoctyl.

In addition to the foregoing aliphatic groups, groups containing hetero-atoms, such as oxygen, sulfur or nitrogen, in the chain may also be used. Examples of these radicals are ethers of the alkoxyalkyl type, including methoxyhexyl and

ethoxydecyl. Alkylthioalkyl groups include methylthiododecyl groups. Primary, secondary and tertiary amines may also serve as the terminal portion of the hydrophobic group. These include diisopropylamino, methylaminoethyl, and aminodecyl.

5 The aryl groups include the phenyl and naphthyl groups and substituted derivatives. Substituted alkyl derivatives include toluyl, xylyl, pseudotumyl, mesityl, isodurenyl, durenyl, pentamethylphenyl, ethylphenyl, n-propylphenyl, cumyl, 1,3,5-triethylphenyl, styryl, allylphenyl, diphenylmethyl, triphenylmethyl, tetraphenylmethyl, 1,3,5-triphenylphenyl. Nitro- and halo-substituted may be exemplified by chloronitrophenyl, chlorodinitrophenyl, dinitrotoluol, and trinitroxylyl. 10

Amine-substituted components include methylaminotoluyl, trimethylaminophenyl, diethylaminophenyl, aminomethylphenyl, diaminophenyl, ethoxyaminophenyl, chloroaminophenyl, bromoaminophenyl and phenylamino- 15 phenyl. Halo-substituted aryl groups include fluoro-, chloro-, bromo-, iodophenyl, chlorotoluyl, bromotoluyl, methoxybromophenyl, dimethylaminobromophenyl, trichlorophenyl, bromochlorophenyl, and bromoiodophenyl.

Groups derived from aromatic carboxylic acids are also useful. These include methylcarboxylphenyl, dimethylaminocarboxyltoluyl, laurylcarboxyltoluyl, nitro- 20 carboxyltoluyl, and aminocarboxylphenyl. Groups derived from substituted alkyl esters and amides of benzoic acid may also be used. These include aminocarboxylphenyl and methoxycarboxylphenyl.

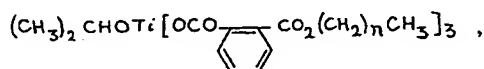
Titanates wherein R' is an epoxy group include tall oil epoxides (a mixture of 6 to 22 carbon alkyl groups) containing an average of one epoxy group per 25 molecule and glycidol ethers of lauryl or stearyl alcohol.

Substituted naphthyl groups include nitronaphthyl, chloronaphthyl, aminonaphthyl and carboxynaphthyl groups.

Specific compounds which have been prepared and found operative in the practice of the instant invention include:

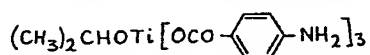
30 $(\text{CH}_3)_2\text{CHOTi}[\text{OCO}(\text{CH}_2)_{14}\text{CH}(\text{CH}_3)_2\text{OCOC}(\text{CH}_3)=\text{CH}_2]_3$ 30

$(\text{CH}_3)_2\text{CHOTi}[\text{OCO}(\text{CH}_2)_{14}\text{CH}(\text{CH}_3)_2][\text{OCOC}(\text{CH}_3)=\text{CH}_2]_2$;

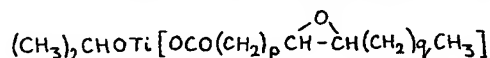


where n is greater than 8 and less than 15;

35 $[(\text{CH}_3)_2\text{CHOTi}[\text{OCO}(\text{CH}_2)_{14}\text{CH}(\text{CH}_3)_2\text{OCOC}_{14}\text{H}_{28}]_3$ 35
 $(\text{CH}_3)_2\text{CHOTi}[\text{OCO}(\text{CH}_2)_{16}\text{CH}_3]_3$;



$(\text{CH}_3)_2\text{CHOTi}[\text{OCO}(\text{CH}_2)_3\text{NH}_2]_3$; and



where the sum of p + q is more than 6 and less than 18.

40 The inorganic materials may be particulate or fibrous and of any shape or particle size, the surfaces of which are reactive with the hydrolyzable group of the organo-titanium compound by means of hydroxyl groups, or adsorbed water, or both. Examples of inorganic reinforcing materials include metals, metal oxides, 45 clay, carbon black, calcium carbonate, barium sulfate, silica, mica, glass and asbestos. Reactive inorganic material examples include the metal oxides of zinc, magnesium, lead, and calcium and aluminum, iron filings and turnings, and sulfur. Examples of inorganic pigments include titanium dioxide, iron oxides including yellow iron oxide, zinc chromate, ultramarine blue. As a practical matter, the

particle size of the inorganic material should not be greater than 1 mm, preferably from 1 micron to 500 micron.

It is imperative that the organic titanate be properly admixed with the inorganic material so as to permit the surface of the latter to react sufficiently. The optimum amount of the titanate to be used is dependent on the effect to be achieved, the available surface area of and the bonded water in the inorganic material.

Reaction is facilitated by admixing under the proper conditions. Optimum results depend on the properties of the titanate, namely, whether it is a liquid or solid, and its decomposition and flash point. The particle size, the geometry of the particles, the specific gravity, the chemical composition, among other things, must be considered. Additionally, the treated inorganic material must be thoroughly admixed with the polymeric medium. The appropriate mixing conditions depend on the type of polymer, whether it is thermoplastic or thermosetting, its chemical structure, etc., as will be readily understood by those skilled in the art.

Where the inorganic material is pretreated with the organic titanate, it may be admixed in any convenient type of intensive mixer, such as a Henschel or Hobart (Trade Mark) mixer or a Waring blender. Even hand mixing may be employed. The optimum time and temperature is determined so as to obtain substantial reaction between the inorganic material and the organic titanate. Mixing may be performed under conditions at which the organic titanate is in the liquid phase, at temperatures below the decomposition temperature. While it is desirable that the bulk of the hydrolyzable groups be reacted in this step, this is not essential where the materials are later admixed with a polymer, since substantial completion of the reaction may take place in this latter mixing step.

Polymer processing, e.g., high shear mixing, is generally performed at a temperature well above the second order transition temperature of the polymer, desirably at a temperature where the polymer will have a low melt viscosity. For example, low density polyethylene is best processed at a temperature range of 350° to 450°F; high density polyethylene from 400° to 475°F; polystyrene from 450° to 500°F; and polypropylene from 450° to 550°F. Temperatures for mixing other polymers are known to those skilled in the art and may be determined by reference to existing literature. A variety of mixing equipment may be used, e.g., two-roll mills, Banbury mixers, double concentric screws, counter or corotating twin screws and ZSK type of Werner and Pfaudler and Busse mixers.

When the organic titanate and the inorganic materials are dry-blended, thorough mixing and/or reaction is not readily achieved and the reaction may be substantially completed when the treated filler is admixed with the polymer. In this latter step, the organic titanate may also react with the polymeric material if one or more of the R' groups is reactive with the polymer.

To illustrate further the invention, attention is directed to the following examples:

Example A: Preparation of Organo-Titanate Esters.

One mole of tetraisopropyl titanate is admitted to a vessel equipped with an agitator, an internal heating and cooling means, a vapor condenser, a distillate trap and liquid-solid feed input means. Agitation is commenced with the tetraisopropyl titanate at room temperature. Liquid isostearic acid is metered into the vessel at a controlled rate so that the exothermic reaction is maintained below about 350°F until 3.19 moles of the acid are added. The isopropanol is removed from the reaction product by distillation at 150°C at 50 mm Hg to remove potentially objectionable volatiles.

The organic titanate thus produced has an average of 3.19 moles of isostearate per molecule. This material is hereinafter referred to as the "isostearate 3.19 ester." The ester structure is determined by ascertaining the isopropanol liberated from the reaction and the residual isostearic acid. It is found that about from 3.1 to 3.3 moles of isopropanol are recovered in the typical run. Substantially no unreacted isostearic acid is detected. The physical properties of the ester are:

Specific Gravity at 74°F	0.944
Flash Point (COC), °F	315
Viscosity, LV, at 74°F, cps.	120

Pour Point, °F	Below -5
Decomposition Point, °F	Above 400
Gardner Color	15 Max
Appearance	Reddish Oily Liquid

- 5 The above run is repeated, except that instead of adding 3.19 moles of the isostearic acid, 1.0, 2.0 and 3.0 moles are added. This results in the formation of mixtures of isopropyl isostearate titanates having an average number of isostearate groups per molecule of 1, 2 and 3 moles, respectively. 5

- 10 **Example B.**
This example demonstrates the effect of admixing the isostearate 3.19 ester with various fillers dispersed in naphthenic oil. The fillers employed include calcium carbonate, calcined clay, high surface area silica, carbon black, and chemically oxidized carbon black. The effect of varying percentages of the titanate ester on the viscosity of the end product is also shown in the data below: 10

Fillers Dispersed in Mineral Oil (Naphthenic Oil)

	1	2	3	4	5	6	7	8
CaCO ₃ , parts by wt.	15	35	50	50	70	75		
Mineral Oil,	85	65	50	50	30	25		
Titanate Ester, % on Filler	—	—	—	0.5	0.5	0.5		
Brookfield Viscosity at 25°C, cps.	82	1,600	32,500	280	2,320	12,600		
Calcined Clay, parts by wt.	30	30	50	65				
Mineral Oil,	70	70	50	35				
Titanate Ester, % on Filler	—	3	3	3				
Brookfield Viscosity at 25°C, cps.	30,000	215	1,280	22,000				
Hi Surface area silica, parts by weight	5	10	15	20	5	10	15	20
Mineral Oil, "	95	90	85	80	95	90	85	80
Titanate Ester, % on Filler	—	—	—	—	1	1	1	1
Brookfield Viscosity at 25°C, cps.	120	615	5,750	7,000	114	520	4,700	4,100
Hi Surface area silica, parts by weight	5	10	15	20	5	10	15	20
Mineral Oil, "	95	90	85	80	95	90	85	80
Titanate Ester, % on Filler	2	2	2	2	3	3	3	3
Brookfield Viscosity at 25°C, cps.	92	465	4,200	3,800	86	345	3,000	3,500
Commercially Oxidized Carbon Black, pts. by wt.	10	15	20	25	10	15	20	25
Mineral Oil,	90	85	80	75	90	85	80	75
Titanate Ester, % on Filler	—	—	—	—	3	3	3	3
Brookfield Viscosity at 25°C, cps.	462	1,612	5,000	16,800	350	1,125	3,300	7,700

A regular grade of carbon black was chemically oxidized *in situ* to convert carboxyl groups to hydroxyl groups. The results are shown below:

	Type of Treatment	Brookfield Viscosity at 77°F, cps. of Dispersion	
5	Carbon Black (untreated)	9,200	5
	Carbon Black (5% chemically oxidized)	15,800	
10	Carbon Black (5% chemically oxidized and treated with 3% titanate ester)	2,700	10

The aforesaid data clearly show that materials reacted *in situ* with the titanate ester make dispersions having substantially reduced Brookfield viscosities. Marked reductions in viscosity are shown particularly with the calcium carbonate, calcined clay, and carbon black. This reduced viscosity greatly enhances the ease of mixing these fillers with the organic-type materials and results in improved dispersion at lower energy requirements for mixing.

Example C.

This example, using the procedures of Example B, shows the effect of other organic titanate compounds on the viscosity of calcium carbonate in naphthenic mineral oil dispersions. The compositions tested contain 50 parts by weight of oil, 50 parts of precipitated calcium carbonate and 0.5% (based on CaCO_3) of the titanate esters. The results are shown below:

	Titanate Ester	Brookfield Viscosity at 72°F \pm 3%	
25	None	32,500	25
	Monoisopropyl diisostearyl, acryl	188	
	Monoisopropyl trimonococo, phthaloyl	152	
	Monoisopropyl diisostearyl; methacryl	175	
	Monoisopropyl dimethacryl, isostearyl	175	
30	Monoisopropyl tri-2-aminoacetyl	34,600	30
	Monoisopropyl tripropionyl	30,000	

The above table shows the dramatic effect on viscosity of the titanate esters of the invention. The last two examples fall outside of the invention since all the non-hydrolyzable groups are short chain radicals. In such cases, the viscosity of the CaCO_3 filled oil is substantially unaffected.

The effect of isostearic isopropyl titanates on the dispersion and chemical reactivity of zinc oxide is shown in the following examples:

Example 1: Effect of Isostearate Esters on the Dispersion of Zinc Oxide in an Organic Medium.

	Formulation	Parts by Weight	
40	Zinc oxide (-325 mesh, S.A. 5.3 m ² /gm.)	90	40
	Hydrocarbon oil (Naphthenic process oil)	7	
	Ester as shown below	3	

PENETRATION (ASTM TEST No. D1231) at 74°F

	Days after Mixing	Isostearate Esters					
		1.0 mol.	2.0 mols.	3.0 mols.	3.19 mols.*	3.70 mols.	
5	0	(Could not make dispersion)	160	170	165	615	5
	2		125	140	150	—	
	4		89	105	118	—	
	6	„	85	105	115	—	
10	7	„	80	90	112	—	10

* The "isostearate 3.19 ester"

The greater the degree of penetration, the more fluid is the mix. After aging, the isostearate 3.19 ester gives the most desirable penetration characteristics. It can be seen by the data that, desirably, the most stable fluid mix is obtained with three or slightly more mols of isostearate in the titanate ester.

The dispersion made with the isostearate 3.19 ester was compared with the same zinc oxide in the untreated powder form in a natural rubber compound except that 10% less zinc oxide was used when making the rubber compound with the treated zinc oxide dispersion described in Example 1. The formulation and test results are shown in Example 2, as follows:

Example 2: Effect of Treated Zinc Oxide Dispersion in a Natural Rubber Compound.

FORMULATION

	Zinc Oxide Powder (pts. by weight)	90% Zinc Oxide Dispersion (Example 1)	
25	Natural Rubber	100	25
	Peptizer—REOGENT (Trade Mark)	2	
	Stearic Acid	2.5	
30	Zinc Oxide Powder	3.5	30
	90% Zinc Oxide Dispersion (isostearate 3.19 ester)	—	
		3.5	
	HAF Black (high abrasive furnace black) (N330)	45	
35	Sulfur	2.5	35
	Ultra-Accelerator e.g. thiuram sulfide or a dithiocarbonate (AMAX (Trade Mark) No. 1)	.5	
		.5	

PHYSICAL PROPERTIES

Stress PSI at 300% Elongation (S), Tensile Strength PSI (T), % Elongation (E), Hardness, Shore A (H).

5	Press Cures at 290°F	S	T	E	H	S	T	E	H	5
	15 min.	1120	2850	500	55	1380	3810	550	57	
	45 min.	1380	2890	460	59	1640	3780	520	59	
	60 min.	1460	2900	460	59	1520	3610	500	60	

RATE AND STATE OF CURE

10 Rheometer at 290°F, 60 Sec. Preheat, 10
60 Min. Motor, 100 Range, 3° Arc

		Zinc Oxide Powder (pts. by weight)	90% Zinc Oxide Dispersion (Example 1)	
15	Max. Torque	56.2 in./lbs.	77 in./lbs.	15
	Min. Torque	15 "	22.5 "	
	T90 (% degree of cure)	19.5 minutes	17.5 minutes	
	T95 "	24 "	22 "	
	T2 "	2.2 "	2.7 "	

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PROCESS TIME

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Mooney Scorch at 250°F.

	Minutes	5	Minutes	5	
Time Scorch Begins					
Time to 5 Point Rise		3		3	
Total Time		8		8	
25 Rise Last Minute		3		3.5	25
Plasticity		16		35	

30

The table in Example 2 shows the great improvement in physical properties of a natural rubber compound achieved by the use of the isostearate 3.19 ester treatment of the zinc oxide surface even when 10% less zinc oxide is used. Tensile strength is increased by 30%, elongation by 10%, stress at 300% elongation by 10%. It is significant that hardness is not affected. The Mooney plasticity is more than doubled at 250°F, while the rheometer data at 290°F shows that the treated zinc oxide provides a tighter cure.

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The following Example 3 shows the improvement in properties obtained when using the zinc oxide dispersion made with the isostearate 3.19 ester of Example 1 in an oil-black extended SBR (styrene-butadiene rubber) compound:

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Example 3: Effect of Treated Zinc Oxide Dispersion in a Styrene-Butadiene Rubber Compound.

FORMULATION

	Compound SBR, Oil-Black Extended	Zinc Oxide Powder (pts. by weight)	90% Zinc Oxide Dispersion (Example 1)	
5	PP 1849 (Phillips Petroleum SBR)	245	245	5
	Zinc Oxide	3	—	
10	90% Zinc Oxide Dispersion (isostearate 3.19 ester)	—	3	10
	Anti-Oxidant (Flexzone 3C)	1	1	
	Accelerator—CBTS	1.3	1.3	
	Sulfur	2.1	2.1	
	Accelerator—TMTM	0.55	0.55	
15	Ultra-Accelerator (Vultac #5)	1.2	1.2	15
	Resin Modifier Nebony 100	10	10	
	Stearic Acid	1	1	

PHYSICAL PROPERTIES

20 Stress PSI at 300% Elongation (S), Tensile Strength PSI (T), % Elongation (E),
Hardness, Shore A (H). 20

Zinc Oxide Powder (pts. by weight)					90% Zinc Oxide Dispersion (Example 1)					
25	Press Cures at 307°F	S	T	E	H	S	T	E	H	25
	30 min.	1175	2775	600	59	1325	2929	580	59	
	Press Cures at 280°F									
	40 min.	1240	2800	580	60	1350	2700	530	61	

30

RATE AND STATE OF CURE 30

Rheometer at 280°F, 60 Sec. Preheat,

60 Min. Motor, 50 Range, 1° Arc

Max. Torque 25.75 in./lbs. 25.75 in./lbs.

Min. Torque 5.75 „ 5.65 „

35

TS—2 9.5 minutes 8.25 minutes 35

TC—90 22.5 „ 21.75 „

RATE AND STATE OF CURE Continued

Rheometer at 340°F, 60 Sec. Preheat,

12 Min. Motor, 50 Range, 1° Arc

Max. Torque 21.1 in./lbs. 22.8 in./lbs.

Min. Torque 5.4 „ 5.1 „

TS—2 2.15 minutes 1.9 minutes

TS—90 3.9 „ 3.7 „

PROCESS TIME

Mooney Data at 212°F

Initial 50.5 51.5

1.5 minutes 40.5 41.5

4.0 minutes 36.5 37.5

The data in Example 3 show an equal or improved condition of physical properties with the use of 10% less of zinc oxide. In actual processing, it has been observed that the isostearate 3.19 ester treated zinc oxide dispersion of Example 1 is incorporated into the rubber compound in about one-fourth to one-fifth of the time otherwise required for untreated zinc oxide powder. Additionally, the treated zinc oxide powder was non-dusty.

The above data also show that the compound which contains the treated zinc oxide dispersion has a higher degree of reactivity as well as a tighter final cure, as evidenced by the increase in torque, as compared to the untreated zinc oxide.

The following Examples 4, 5 and 6 illustrate the effectiveness of isostearate 3.19 ester in reducing the viscosity of dispersions of various inorganic solids in a hydrocarbon oil.

The dispersion of zinc oxide in a hydrocarbon oil results in a greatly reduced viscosity when it is reacted with isostearate 3.19 ester, as can be seen in the following Example 4:

Example 4.

Parts by Weight

Zinc Oxide	50	50
Naphthenic Process Oil	50	47.5
Isostearate 3.19 ester	0	2.5
Brookfield Viscosity at 74°F cps (centipoises)	460,000	80,000

The reduction in viscosity of the zinc oxide dispersion in a hydrocarbon oil by the *in situ* reaction with the isostearate 3.19 ester was 83%.

The viscosity of a dispersion of titanium oxide is similarly reduced by the isostearate 3.19 ester, as shown in the following Example 5:

Example 5.

		Parts by Weight	
5	Titanium Dioxide	50	50
	Naphthenic Process Oil	50	47.5
	Isostearate 3.19 Ester	0	2.5
	Brookfield Viscosity at 74°F cps.	110,000	900

The reduction in viscosity of the titanium dioxide dispersion in a hydrocarbon oil by the *in situ* reaction with the isostearate 3.19 ester was 99%.

The viscosity of a dispersion of carbon black in a hydrocarbon oil is similarly reduced by the same ester, as shown in the following Example 6:

Example 6.

		Parts by Weight	
15	Carbon Black FEF N550	30	30
	Naphthenic Process Oil	70	65
	Isostearate 3.19 Ester	0	3
	Brookfield Viscosity at 79°F, cps.	104,000	46,000

The reduction in viscosity of the carbon black dispersion in a hydrocarbon oil by the *in situ* reaction with the isostearate 3.19 ester was 56%.

The viscosity of a dispersion of calcium carbonate in a liquid epoxy resin is reduced when the isostearate 3.19 ester is added, as shown in the following Example 7:

Example 7.

		Parts by Weight	
25	Calcium carbonate (low oil absorption type)	50	50
	Liquid epoxy resin (epoxide equivalent -185)	50	45
	Isostearate 3.19 Ester	0	5
	Brookfield Viscosity at 74°F, cps.	550,000	110,000

The reduction in viscosity of the calcium carbonate dispersion in liquid epoxy resin by the *in situ* reaction with the isostearate 3.19 ester was 80%.

The viscosity of a dispersion of colloidal silica in a liquid polysulfide rubber is reduced when the isostearate 3.19 ester is added, as shown in the following Example 8:

Example 8.

		Parts by Weight		
5	Colloidal silica (Neosil A)	50	50	
	Liquid polysulfide rubber (Thiokol (Trade Mark) TP-90B)	50	45	5
	Isostearate 3.19 ester	0	5	
	Brookfield Viscosity at 74°F, cps.	8,000	2,250	

10 The penetration of a paste dispersion of calcium carbonate in a liquid (Thiokol) polysulfide rubber was increased when the isostearate 3.19 ester was added. Alternatively, when the amount of calcium carbonate in the dispersion was increased 50%, the penetration remained the same, through the addition of an increased amount of the isostearate 3.19 ester. These effects are shown in the following Example 9:

Example 9.

		Parts by Weight			
15	Calcium carbonate (Purecal SC)	200	200	300	
	Polysulfide liquid rubber (Thiokol LP-32)	100	100	100	
	Isostearate 3.19 ester	0	4	15	
	Penetration (ASTM Test No. D-1321)	45	82	46	

20 The dispersions of Examples 4 through 9 were initially prepared without the isostearate 3.19 ester by preblending the pigment or filler with the organic liquid medium using a Pony mixer. This preblend was then ground on a three-roll mill to make the final dispersion. Viscosity or penetration measurements were made for a control comparison.

25 The effect of the titanate ester was then evaluated by a second set of tests in which the titanate ester was added to the organic liquid medium and the dispersion made as described before. Viscosity measurements made on the new batches disclosed very considerable and significant reduction in viscosity demonstrating that the isostearate esters of the invention are effective with a variety of inorganic materials and in different liquid organic media. This reduction in viscosity indicates that inorganic materials treated by the processes disclosed herein can (1) be used in higher loadings, (2) become more completely dispersed in the organic medium and in the end product, and (3) create viscosity levels which lend themselves to improved manufacturing processes such as reduced energy levels for mixing or for pumping of such dispersions.

35 These examples demonstrate that the inorganic materials do not have to be pretreated and the surface modification can be accomplished *in situ* by the use of the isostearate titanate ester. Also, the ester is effective in reducing viscosity of a wide variety of inorganic materials in a wide variety of organic media.

40 The following Example 10 shows the effectiveness of isostearate 3.19 ester in producing a shorter mixing time and lower viscosity in a dispersion of magnesium oxide in hydrocarbon oil. In actual mixing, it is necessary to add the magnesium oxide to the hydrocarbon oil in increments in order to obtain the maximum degree of inorganic to organic loading in the shortest possible time. The table below outlines this procedure and the results obtained:

Example 10.

		Parts by Weight	
	Magnesium Oxide	55	55
	Naphthenic Process Oil	45	42
5	Isostearate 3.19 ester	0	3

		Increment Addition No.	Weight	Time in Minutes	
		1	16.67	0	0
		2	8.33	0.5	0.5
10		3	8.33	1.0	1.0
		4	8.33	2.0	2.0
		5	5.00	4.0	2.5
		6	4.17	4.5	3.0
		7	4.17	5.0	3.5
15			55.00		
	Time to Complete Dispersion			6.5	4.5
	Penetration (ASTM Test No. D—1321)			160	230

20 The resultant dispersion was therefore made 30% softer while requiring 31% less mixing time.

Example 11.

25 The effect of reacting the isostearate 3.19 ester with calcium carbonate (a precipitated small particle grade) *in situ* in low density polyethylene (LDPE, sp.g. 0.918) is shown in the table below. This table compares the melt viscosity vs. time in making a dispersion of calcium carbonate in low density polyethylene having a melt index of 7, when 70 parts of calcium carbonate are blended with 28 parts of LDPE.

30 In these experiments, 2.85% of the isostearate 3.19 ester (based on the calcium carbonate) was added before starting the mixing in a Brabender high intensity mixer. The mixing was carried out at a maximum temperature of 200°F, and at 82 RPM, using a 5 Kg weight on the ram, while the melt viscosity was observed by measuring the torque applied to the mixer in gram meters.

35 Similar experiments were made when the isostearate ester was omitted, and when two other dispersion aids, namely, aluminum tristearate and polyglycerol 400 mono-oleate, were used at the same concentration, namely, 2.85% (based on CaCO₃). The results are also shown in the following table:

		Torque Readings (gms.-meter ²)					
		Time (seconds)		90	120	150	190
Additives		30	60				
5	Isostearate 3.19 Ester	1250	900	900	900	750	750
	No Additive	2000	2000	1900	1750	1750	1750
	Aluminum Tristearate	1900	1400	1300	1250	1250	1250
	Polyglycerol 400 Mono-Oleate	2150	1400	1150	1000	1000	1000

When no additive was employed, the torque after 30 seconds of mixing was 2,000 gm.-sq. meter, and after 190 seconds was 1750.

When the isostearate 3.19 ester was used, the torque had dropped to 1250 gm.-sq. meter in 30 seconds, and was 750 at 190 seconds, showing the great reduction in melt viscosity in a very short time.

When the aluminum tristearate was used, the torque had dropped to 1,900 gm.-sq. meter after 30 seconds, and to 1,250 after 190 seconds, appreciably higher than the titanate ester. The polyglycerol 400 mono-oleate additive produced a torque of 2,150 gm.-sq. meter after 30 seconds of mixing, and a torque of 1,000 after 190 seconds of mixing.

The effectiveness of the isostearate 3.19 ester as a dispersion agent was also demonstrated by an additional test in which the 70% CaCO₃ dispersion was mixed with additional LDPE polymer in the ratio of 1 to 9, and then made into film by blown-film extrusion. The resulting film was then examined visually to measure the number of remaining agglomerated particles per square foot. When no dispersion additive was employed, there were 312 agglomerates per square foot. When the titanate ester was employed, the number of agglomerates dropped to 16 per square foot.

Example 12.

This example is similar in procedure to that described in Example 11. Titanium dioxide (rutile) was used as the inorganic dispersed phase in the same LDPE as used in Example 11. The dispersion was made at 75 parts TiO₂ using 2.67% dispersion additive (based on the TiO₂), and 23 parts of LDPE.

The following table shows that with no dispersion additive the torque on the Brabender mixer after 30 seconds was 2,250 gm.-sq. meter, and after 180 seconds had dropped to 1,100. When the isostearate 3.19 ester was added, the torque after 30 seconds was reduced to 1,250 gm.-sq. meter, and after 180 seconds was 750.

Torque Readings (gms.-meter²)

	Additive	Time (seconds)		90	120	150	180	
		30	60					
5	Control No Additive	2250	1750	1250	1250	1150	1100	5
	Isostearate 3.19 ester	1250	900	900	900	750	750	
	Polyglycerol 400 Mono-Oleate	2000	1500	1250	1000	1000	1000	
	Aluminum Tristearate	1000	750	750	600	500	500	

10 When the TiO₂ dispersion was reduced in concentration to 7.5% and blow film made, the number of agglomerates per square foot without additive was 600, and with the isostearate ester the agglomerate count was reduced to 150 per square foot. There was also a very noticeable increase in opacity and whiteness.

15 It can also be seen from the table that in the case of TiO₂ dispersion the polyglycerol 400 mono-oleate was inferior, while the aluminum stearate was superior to the titanate ester as a dispersion aid.

Example 13.

20 This example is similar in procedure to Examples 11 and 12. The inorganic dispersed phase was yellow iron oxide and 50 parts were used with 40% dispersion additive (based on the iron oxide), and 48 parts of LDPE. The following table shows the results.

Torque Readings (gms.-meter²)

	Additive	Time (seconds)		90	120	150	180	
		30	60					
25	Control No Additive	2500	1750	1000	1000	1000	1000	25
	Isostearate 3.19 ester	2500	1400	850	750	750	750	
	Aluminum Tristearate	2000	1250	850	800	800	800	
	Polyglycerol 400 Mono-Oleate	2000	1100	1000	900	800	800	

30 When no dispersion additive was employed, the torque on the Brabender was 2,500 gm.-sq. meter after 30 seconds, and 1,000 after 180 seconds. When the isostearate 3.19 ester was added, the torque after 30 seconds was also 2,500 gm.-sq.

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